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KINETICS OF BURNING MANGANESE, SILICON
AND SULFUR OUT OF MOLTEN IRON

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Investigation of the velocity of burning carbon out of a steel bath, previously conducted by the authors, demonstrated that kinetically the process is of a diffusion character ^{dc} and, under the conditions of a high-frequency induction furnace, the reaction proceeds on the surface separating metal from air. It was shown that the velocity of carbon burning out may be expressed by the equation of the first order reaction:

$$-\frac{dc}{dt} = kc, \quad (1)$$

Where c - concentration of carbon in molten iron. This formula may be compared with the equation for Fick's diffusion law:

$$-\frac{dn}{dt} = k'sc, \quad (2)$$

where n - total quantity of carbon, s - area of contact between metal and air, c - concentration of carbon in metal and k^1 - the constant of proportionality depending on the intensity of stirring (it is assumed that the carbon concentration at the surface of metal is zero). Division of both parts of this equation by the volume or the weight of metal proportional to the volume gives:

$$-\frac{dc}{dt} = \frac{k^1c}{m} \cdot c, \quad (3)$$

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where m is the weight of metal.

Comparison of equations (1) and (3) leads to the equality:

$$\frac{K's}{m} = K, \quad (4)$$

from which it follows that the velocity constant k is a function of the ratio between the metal-air contact area and the weight of the metal. Equation (4) proved to be approximately correct for the process of carbon burning-out in a sufficiently wide range of ratios $\frac{S}{m}$.

The purpose of the present work was investigation of the removal velocities for manganese, silicon and sulfur dissolved in molten iron. It was interesting to find out if the regularities deduced for the process of carbon burning-out might be applied also to elimination of other elements. It must be noted that technical literature does not mention any investigation of the burning-out kinetics of manganese, silicon, sulfur and other admixtures dissolved in molten iron. In contrast with the decarburization process, which is the subject of numerous experimental and theoretical investigations, there is not a single work on the burning-out mechanism of other elements.

Burning-out conditions for the majority of elements, dissolved in the steel bath, are substantially different from the conditions for carbon burning-out. Carbon monoxide formed in the latter case leaves the reaction zone right after its evolution from metal. But the oxides, obtained in interaction of oxygen with elements dissolved in iron, enter the slag and remain in contact with molten metal. Presence of the slag phase complicates the burning-out reaction. Therefore it is expedient to study such processes under the most simple conditions, i.e., in the absence of the slag phase.

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Such conditions were observed in experiments by removing slag with an iron rod. Otherwise, the investigation was conducted in the manner already described in the article on the kinetics of carbon burning-out (Journal of Physical Chemistry, 9, 1947).

The first series of experiments for studying burning-out velocities of manganese, conducted with Armco iron (weight of metal 7 kilograms), showed that this case is also satisfied by the equation for the first order reaction.

Experimental melts were conducted at various temperatures, and no noticeable connection was detected between temperature and the value of the velocity constant. This factor, in addition to confirming the applicability of equation (1), also confirms the diffusion character of the process.

Investigation of the burning-out velocity for silicon was considerably hampered by the viscous film of oxides which could not be readily removed in every case. For this reason results obtained were not so well defined as those for the case of manganese. The average value of the velocity constant for silicon burning-out was determined as equal to $1.20 \cdot 10^{-2} \text{ min.}^{-1}$. This value is close to the value of the velocity constant for manganese burning-out ($1.56 \cdot 10^{-2} \text{ min.}^{-1}$), which again confirms the concept of diffusion character accepted for the kinetics of processes of burning admixtures out of the steel bath, since usually the velocity constants of chemical reactions greatly differ from each other, while the diffusion coefficients of different substances in the same solvent differ very insignificantly from each other.

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One melt was conducted without removing slag from the metal surface. In this case the molten iron was at once covered with a viscous film of acid ~~slag~~ ^{slag} which became more and more fluid, enriched by ferrous oxide formed as a result of metal oxidation. After approximately one hour, the slag was unable to stay on the metal surface on account of its high fluidity. Graphical representation of the burning-out process shows that the kinetics of silicon burning-out still conforms to equation (1) even when the metal is covered with slag. However, the reaction proceeds considerably more slowly in this case. The velocity constant during this period was $0.74 \cdot 10^{-2} \text{ min}^{-1}$. This may be explained by the fact that the slag film hampers the access of oxygen to such an extent that silicon concentration at the surface varies from zero. As soon as the metal surface became clear of slag, the velocity constant sharply increased to $1.78 \cdot 10^{-2} \text{ min}^{-1}$. These results may explain the retarded burning-out of silicon observed in some moltings.

On the basis of experimental data on equilibrium in the iron-sulfur system accumulated up to the present, it is possible to prove thermodynamically that the burning-out process of sulfur cannot occur in the volume of metal but is only possible on the surface of metal-air separation. In order to study the velocity of sulfur burning-out and to compare it with the rate of carbon burning-out, determined under similar conditions, three moltings were conducted. The weight of metal in each melt was 7 kilograms. In addition, one melting was performed with iron containing 0.28% of carbon. Analysis of results obtained showed that carbon has no noticeable effect on the rate of sulfur burning-out which (rate) remains the same as in the absence of carbon. Further it was found that these results are well defined and that equation (1) is also applicable in this case. Values for the velocity constants of all melts were similar, which shows that the

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the temperature coefficient of the burning-out process of sulfur is very small. This conclusion is in agreement with results previously obtained for the kinetics of burning-out processes of carbon, manganese and silicon.

Since, according to previously accepted assumptions, rates of burning-out admixtures of the steel bath are determined by the rates of diffusion, the comparison of burning-out velocities of various elements may give an idea of their relative coefficients of diffusion. Thus, if the diffusion coefficient of one element is known, the absolute values for diffusion coefficients of other elements may be calculated. Under conditions of the induction furnace metal is continuously stirred and therefore the concentration of dissolved elements is uniform in the entire mass of metal. It is known that the velocity constants of the chemical reactions of burning admixtures out of molten iron are very high (this follows, for example, from data on Bessemer meltings) and advance of these processes is limited by the diffusion of dissolved elements through a thin non-stirrable surface layer of metal.

With these considerations equation (3) may be written in the following form:

$$-\frac{dc}{dt} = \frac{D_s}{m} \frac{c}{\delta} \quad (5)$$

where D is the coefficient of diffusion and δ is the effective thickness of the non-stirrable film of metal at the surface,

Comparison of equations (5) and (1) shows, that the formula which follows expresses the relationship between the experimentally determinable velocity constant of burning-out and the diffusion coefficient, area of the metal-air surface of separation, metal mass and thickness of the non-stirrable layer:

$$K = \frac{Dc}{m\delta} \quad (6)$$

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Thus, comparison of the velocity constants of burning-out of various elements under similar conditions gives a possibility for determining their diffusion coefficients. Before calculating the diffusion coefficients it should be indicated that dissolving processes of elements in molten iron also must be described by an expression analogous to the equation (1):

$$\frac{dc}{dt} = K(c_s - c), \quad (7)$$

where c_s is the concentration of saturated solution and c - the concentration in the time interval t .

According to these assumptions the velocity constant of dissolving in equation (7) must be identical to the velocity constant of burning-out.

J. Chipman and D. Murphy (Trans. A.J.M.E., 116, 179, 1935), studying the solubility of nitrogen in liquid iron, also determined its dissolving velocity. They demonstrated that the velocity of nitrogen dissolving in liquid iron is actually expressed by equation (7), and found the value of the velocity constant. The average weight of metal in their experiments was 73 grams and the average value of the velocity constant amounted to 2.6 hours⁻¹. The diameter of the crucible, in which meltings were conducted, was 27 millimeters. Taking into consideration these data and using equation (4), the authors determined the value of K' . For that purpose, the velocity constant was expressed in minutes, $\frac{2.6}{60} = 0.043 \text{ min.}^{-1}$, the area of nitrogen contact with liquid metal was calculated, $S = 3.14 \cdot 1.35^2 = 5.8 \text{ cm}^2$, and the values obtained were substituted into the equation (4):

$$K' = \frac{0.043 \cdot 73}{5.8} = 0.53 \frac{\text{g}}{\text{cm}^2 \text{ min.}}$$

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Values of K' also were calculated for carbon, manganese, silicon and sulfur: $K' = 1.56$ for Mn, 1.20 for Si, 0.46 for C and 0.27 for S. Comparison of equations (4) and (5) gives the expression: $K' = \frac{D}{\delta}$, which for manganese may be written as

$$K'_{Mn} = \frac{D_{Mn}}{\delta} \quad (8)$$

and for silicon as

$$K'_{Si} = \frac{D_{Si}}{\delta} \quad (9)$$

Assuming that the value of δ is determined by electrodynamic stirring of metal, being constant for a given furnace, we obtain, dividing the equation (8) by (9):

$$D_{Si} = \frac{D_{Mn} K'_{Si}}{K'_{Mn}}$$

M. Paschke and A. Hautmann (Arch. f. Eisenhüt., 305, 1935) determined experimentally the diffusion coefficients for manganese and silicon in molten iron at 1600 degrees Centigrade. The two coefficients are close to each other, but results for manganese were more dependable, and the above mentioned authors give a numerical value for the diffusion coefficient only in the case of manganese, namely:

$$D_{Mn} = 9.6 \text{ cm}^2 \text{ per 24 hour period.}$$

On the basis of this value the diffusion coefficients were calculated for silicon, nitrogen, carbon and sulfur. Those values are as follows: 7.39 for Si, 3.26 for N, 2.83 for C and 1.66 for S.

Equation (7) also permits calculation of the thickness of the non-stirrable layer δ , which was determined as approximately equal to 0.1 millimeter.

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